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EFFECT OF MICROBIOLOGICAL TREATMENT ON TECHNOLOGICAL PROPERTIES OF CLAYS WITH DIFFERENT MINERALOGICAL COMPOSITIONS (A REVIEW)

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The effect of the bacterial culture *Bacillus mucilaginosus* on the structural-mechanical, flow, drying, and other properties of argillaceous materials of different mineralogical compositions is investigated. Bacterial treatment of clay material increases its degree of dispersion and plasticity and decreases its linear air shrinkage and the drying sensitivity coefficient, which makes it possible to shorten the drying cycle, decrease the quantity of defectives pieces, lower the firing temperature, intensify the sintering process, and increase the strength of molded preforms and finished articles.

The contemporary manufacture of construction materials and products, in particular, those based on argillaceous materials, involves the use of multicomponent mixtures, development of new technologies and upgrade of existing ones, improvement of product quality, production of highly efficient multipurpose articles, and the application of more powerful machinery. In these conditions the economical use of mineral and fuel resources is of primary significance, especially in such energy- and material-consuming sector as the production of ceramics.

Until recently ceramic factories of Belarus produced construction and household ceramics using fire-resistant and high-melting clays from Ukraine and Russia. In recent years, in view of expanding substitution of imported materials, the republic is increasingly using ceramic mixtures based on local materials, mainly due to the high prices of imported analogs and high transportation costs.

Argillaceous materials in Belarus typically have a polymineral composition, in particular, a substantial content of hydromica, as well as impurity minerals, such as quartz, carbonate, and ferrous inclusions, which have a negative impact on the rheological, structural-mechanical, drying, and other properties of ceramic mixtures and on sintering processes. Accordingly, researchers are looking for new, more effective methods for improving the quality parameters of polymineral clays and ceramic mixtures with the aim of fully or partially replacing aluminosilicate materials with local ones and involving in production new deposits of Belarus or those that have not been used before.

The problem of improving the quality of clay materials has long been a focus of attention for leading ceramic scientists who analyzed various methods of treating clays and clay-bearing mixtures. Among these methods is the simple long-term aging under constant moisture and temperature, as well as more complicated methods of treating materials and their mixtures with various chemical reactants.

It is known that long-term aging of argillaceous material modifies its degree of dispersion, improves its plasticity and molding properties, decreases its drying sensitivity, and increases the strength of preforms and finished products. However, using this method at a contemporary ceramic factory requires additional capital investments in building and maintaining premises for storing mixtures and increases the duration of the technological cycle.

In past decades microbiological methods for concentrating argillaceous materials have become widely extended, since they make it possible with slight modifications to the process to achieve substantial results in modifying the natural texture of clays, improving their physicochemical properties and the qualitative parameters of finished products.

The research performed at several centers (D. I. Mendeleev Russian Chemical Engineering University, MoldNIIstrom, NIIsroikeramika), as well as testing these results at several large enterprises, have demonstrated the efficiency of using microorganisms for improving the properties of clays from Ukraine and Belarus. Of all diverse microorganisms, the researchers use only the strains of so-called silicate bacteria, of the species *Bacillus mucilaginosus, subsp. nova: siliceous*.

The authors of patents USSR Inventor's Certif. Nos. 658112, 992483, and 1167168, and [1] propose a method for clay treatment by introducing a suspension of various strains of *Bacillus mucilaginosus* culture for the purpose of increasing the specific surface area and the plasticity number of clay, decreasing its drying sensitivity, and increasing the mechanical strength of non-fired and fired materials.

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Polymineral argillaceous materials from Belarus, which differ significantly in their chemicomineralogical compositions and physicochemical properties, have never yet been the object of such kind of research.

The purpose of our study is to investigate the effect of microbiological treatment of argillaceous materials of different mineralogical compositions on structural-mechanical, rheological, drying, and other properties. It was assumed that microbiological treatment of clay would significantly improve its physicotechnical characteristics and, consequently, expand its areas of application in the ceramic industry.

For our studies we selected argillaceous materials from Belarus deposits differing in their chemicomineralogical compositions, in particular, clays from Gaidukovka (Minsk Region) and Lukoml' and Zapol'e (Vitebsk Region) deposits. All clays are low-melting, polymineral, medium-disperse, and belong to the groups of kaolinite-montmorillonite-hydromica clays. The main minerals contained in these clays are kaolinite, montmorillonite, illite, vermiculite, and glauconite in various ratios; impurities are represented by free quartz, feldspar, and calcite. The averaged chemical composition of the specified clays in given in Table 1.

The biological reactant was the bacterial suspension of the *Bacillus mucilaginosus* culture prepared from dry spore material.

The pure culture of the specified bacteria on an agarized medium forms large colonies, totally transparent, mucous, convex, with smooth edges, resembling clear liquid drops (Fig. 1*a*). The culture is spore-forming and gram-negative. The size of rod-shaped cells is 4 – 7 μm long and 1.2 – 1.4 μm in cross-section; however their size, similarly to other microorganisms, is not strictly constant and depends on the type of nutrient medium. The cells are located at a certain distance from each other, which is due to their having capsules. A capsule is a jelly-like dense material consisting of polysaccharides or polypeptides. As the aging period lengthens (from 10 to 14 days), the rod inside the capsule significantly expands and loses its contour (Fig. 1*b*). With aging of the capsule, lysis starts, i.e., its destruction under the effect of the enzymes arising in the vital activity of the bacteria.

To establish the effect of *Bacillus mucilaginosus* bacteria on the technological properties of the considered clays, bacterial suspensions were prepared with different concentrations of bacterial cells: 150, 100, and 75 million cells per 1 ml. The concentration of bacteria was modified by consecutive dilution of the suspension.

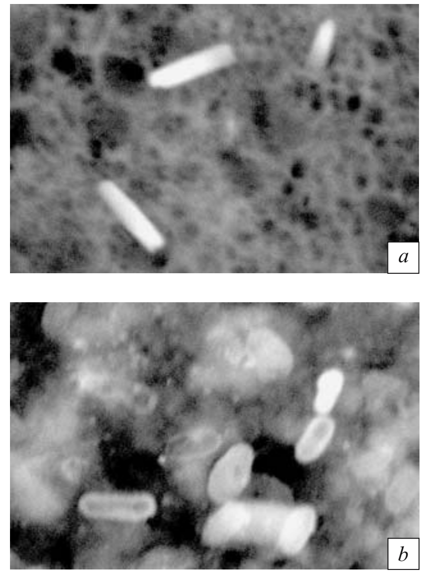

Fig. 1. Electron microscope photos of *Bacillus mucilaginosus* bacterial culture: *a*) young vegetative cells; *b*) cells after 10-day exposure.

The choice of bacteria concentration intervals was based on the published data and preliminary experiments, which made it possible to determine the initial bacteria concentrations that affect the structural characteristics of clays.

Before the experiment clay samples were milled to passing a No. 1 sieve with subsequent moistening and liquefying. The treatment of the argillaceous material was performed by adding 2 ml of bacterial suspension (accordingly, the concentration of bacterial cells is around 300 million cells converted per 100 g of dry matter) to achieve the required moisture of 50%, which did not change after the introduction of bacteria, since the quantity of water was adjusted depending on the quantity of the introduced bacterial suspension. The samples of clay suspensions with introduced bacterial cells were exposed at room temperature and in a thermostat at the temperature of 30 ± 0.5°C for 72, 120, and 168 h. Clay suspensions without bacteria (reference samples) were subjected to the same isothermal exposure.

Based on preliminary studies [2], the optimal conditions of bacterial treatment were selected: moisture of clay suspension — 45 – 50%; concentration of bacterial cells — at least 150 million cells per 1 ml of bacterial suspension; treatment temperature – around 30°C, isothermal exposure duration — 70 – 120 h (3 – 5 days).

TABLE 1

Deposit	Weight content, %								
	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO	CaO	TiO_2	calcination loss
Gaidukovka	55.88	13.80	4.49	0.84	3.75	2.62	8.16	0.48	10.10
Lukoml'	50.38	17.67	7.44	0.68	4.49	2.90	5.46	0.92	9.95
Zapol'e	57.60	14.91	5.51	0.76	3.80	1.89	6.61	0.72	8.20

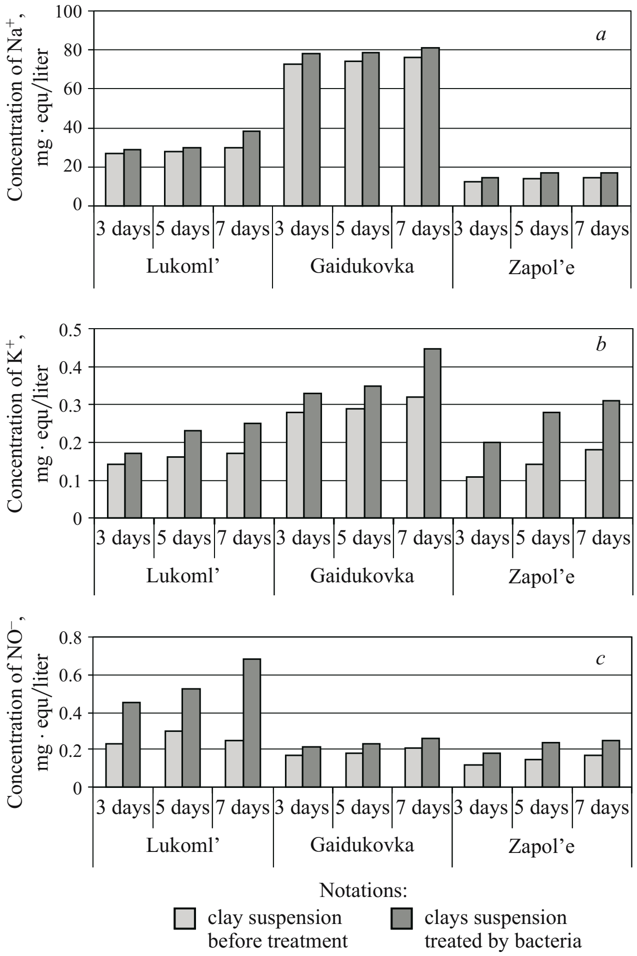

Fig. 2. Dependence of concentration of sodium ions (*a*), potassium ions (*b*), and nitrate ions (*c*) in clay suspensions on the type of clay and duration of bacterial treatment.

It is currently established that minerals are destroyed under the effect of compounds produced by microorganisms. Such compounds include mineral and organic acids, biogenic alkalis, chelate-forming agents, etc. Depending on the cultivation medium conditions and the type of microorganisms, a particular agent can be used for destroying minerals. The process may be accompanied by various reactions, such as hydrolysis, ion exchange, carbonization, formation of complexes, simple dissolution, or chemical restructuring [3].

The specified reactions affect the activity of hydrogen ions and the concentration of mobile metal forms in aqueous suspensions of clays, primarily univalent metals: sodium and potassium.

To estimate the effect of bacteria on the considered clays, after each time interval we measured the pH and the concentration of nitrate ions as well as sodium and potassium ions in the reference and bacteria-treated clay suspensions. The hydrogen index was determined by the pH-meter and the concentration of nitrate ions, potassium and sodium ions, by the ionometric method using ion-selective electrodes. A silver chloride electrode was used as an auxiliary one.

The obtained results on the effect of temperature and silicate bacteria treatment duration on pH indicate (Table 2) that the introduction of bacteria and an exposure at a temperature of 18°C has virtually no effect on pH of all clay samples, which is due to their insufficient life activity at the specified temperature. An increase in the temperature to 30°C intensifies the breeding of bacteria, which leads to a slight but more perceptible modification of pH. A general regularity is observed in all clays: with aging extending from 3 to 5 days pH decreases, whereas after 7 days aging pH slightly increases. Presumably, during the intense growth of bacteria at the initial stages of bacterial treatment, organic and other acids generated by the bacteria decrease the hydrogen index. Later, as the products of metabolism are accumulated, the processes of hydrolysis and reactions between the products of metabolism and minerals intensify, which leads to increasing pH.

The determination of the concentration of sodium ions (Fig. 2*a*) in clay suspensions indicates that this concentration in three samples is different and depends on the chemico-mineralogical composition of the clay and its dispersion. The clay from the Gaidukovka deposit has an increased sodium content and a sufficiently high dispersion, which explains the high concentration of sodium ions in the dispersion medium. It follows from experimental data that the concentration of sodium ions in the reference samples and in samples treated by a bacterial suspension differs insignificantly. As sodium exists in clay mainly in the form of easily soluble salts, the quantity of mobile sodium forms mostly depends on their solubility. A certain increase in the concentration of sodium ions in bacteria-treated clay suspensions can be attributed to the dispersion of clay particles under the effect of bacteria and the increasing area of their contact surface with the solution, and also to the release of sodium ions from the residual sodium-bearing parent rock.

Despite the total content of potassium in clays being higher than that of sodium, the concentration of potassium ions in clay suspensions is significantly lower (Fig. 2*b*). However, in contrast to the concentration of sodium ions, bacterial treatment raises the concentration of potassium ions in suspension 1.5 – 2 times on the average. Since potassium is a component of hydromica minerals, the increasing content of mobile forms of potassium in the treated clay suspension is confirmation of the destruction of minerals by bacteria.

The active growth of bacteria is also corroborated by the results of determining the concentration of nitrate ions (Fig. 2*c*), which can be used to control the process of bacteria

TABLE 2

Deposit	pH of clay suspensions						
	reference	treated at 18°C during, days			treated at 30°C during, days		
		3	5	7	3	5	7
Gaidukovka	8.00	8.00	8.05	8.07	8.07	8.05	8.03
Lukoml’	7.82	7.73	7.75	7.72	7.75	7.64	7.68
Zapol’e	7.84	7.80	7.81	7.81	7.75	7.62	7.71

breeding. The increased content of these ions in biotreated clay suspensions indicates the active life process of the bacteria.

To determine the main physicotechnical characteristics of the considered materials (degree of dispersion, plasticity, drying sensitivity coefficient, linear air shrinkage), the clay suspensions were partly dehydrated through water evaporation.

It was found that the bacterial treatment of clay materials facilitates the dispersion of particles, which is related to the partial destruction of the aluminosilicate component. At the same time, the quantity of particles per volume unit grows and, accordingly, the number of contacts, whose strength is lower than in nontreated materials, increases. This is caused by the effect of compounds released by bacteria in their metabolism. According to the data in [1], the mucus produced by *Bacillus mucilaginosus* bacteria contains around 95% high-molecular polysaccharides, around 5% proteins mostly consisting of amino acids (aliphatic, aromatic, and base), and a small quantity (below 1%) of organosilicon compounds and colloid silicic acid. These materials become adsorbed on clay particles and weaken the strength of contacts, as a consequence of which the mobility of particles grows.

Of great importance in the technology of clay treatment is the size of mineral particles comprising clays. Clay is a polydisperse mineral and the size of argillaceous particles determines its plasticity when mixed with water and several other technological properties.

The granulometric composition (the degree of dispersion) of the considered clays was determined by sedimentation analysis, which is based on the quantitative size distribution of particles depending on their settling time in the aqueous medium. It is established that biological treatment modifies the fractional distribution of particles, which depends on the mineralogical composition of clay and its natural microflora.

All clays typically exhibit an increased quantity of the fine fraction after microbiological treatment. This shows that the activity of bacteria is selective and this concerns finely dispersed fractions. Bacterial treatment has no perceptible effect on medium- and coarse-grain fractions, at least under the specified duration of microbiological treatment. The comparative characteristics of the main properties of argillaceous materials before and after bacterial treatment under optimum conditions (quantity of bacterial cells approximately 300 million cells, treatment temperature 30°C, exposure duration 120 h) are indicated in Table 3.

It should be noted that clays from the Gaidukovka and Lukoml' deposits have rather rich and extended natural microflora. This assumption is corroborated by the analysis of the specified clays for the presence of natural microflora [4], which makes it possible to identify six strains in the Lukoml' deposit and five strains in Gaidukovka clay with morphological characteristics coinciding with the characteristics of *Bacillus mucilaginosus* colonies.

An increased degree of dispersion in argillaceous materials improves such important technological parameter as plasticity. From the data in Table 3 it is seen that the plasticity of clays after bacterial treatment grows on the average 1.4 times, but this effect is ambiguous for various clays.

To compare the effect of bacteria on the structure-formation of disperse clay systems, together with the clay suspension we studied a plastic mixture based on Gaidukovka clay of moisture 18%. Comparing the effect of bacteria on the clay suspension of moisture 50% and the plastic mixture of moisture 18%, it should be noted that bacteria are more active in dispersion systems with a higher moisture, and therefore, their effect is more perceptible. The low viscosity of the suspension and the low plastic strength of this system create favorable conditions for the activity of bacteria, intensify their penetration to mineral particles and into the interlayer space of laminar silicates, and facilitates freer migration of organic products of bacterial metabolism. The emerging organosilicon acids dissolve in free water of the suspension and become more uniformly distributed over the system.

As distinct from suspensions, plastic mixtures typically have higher Bingham viscosity and plastic strength. Such a system is less mobile, since water is fixed under the effect of electrostatic forces of clay particles which are known to carry a negative charge and develop an electric field around themselves. All this impedes the migration of bacteria and their active life. The emerging products of bacterial metabo-

TABLE 3

Main properties	Argillaceous materials of deposits					
	Gaidukovka		Lukoml'		Zapol'e	
	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment
Plasticity number	13.2	21.2	16.7	22.3	12.3	17.2
Linear air shrinkage, %	6.0	5.5	8.1	7.3	6.5	4.5
Drying sensitivity coefficient	1.10	0.77	1.15	0.87	1.10	0.68
Content, %, of particles of size, mm:						
below 0.001	43.20	49.80	59.30	64.90	27.13	32.20
0.001 – 0.005	20.60	19.04	23.10	21.00	22.89	28.10
0.005 – 0.01	18.65	13.00	8.20	4.00	19.50	15.44
0.01 – 0.063	2.79	6.50	7.60	6.50	28.30	22.05
over 0.063	4.80	4.70	3.50	3.60	2.21	2.19

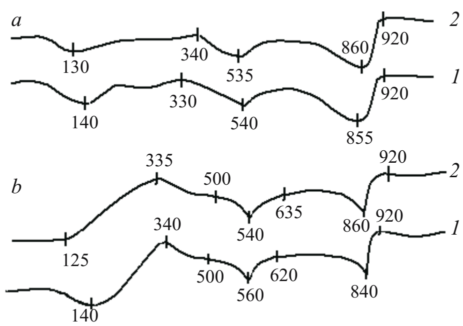

Fig. 3. Differential thermal analysis (°C) curves (*a*) and thermogravimetric weight loss curves (*b*) of clay from Zapol'e deposit before treatment (*1*) and after treatment with bacterial suspension under optimal conditions (*2*).

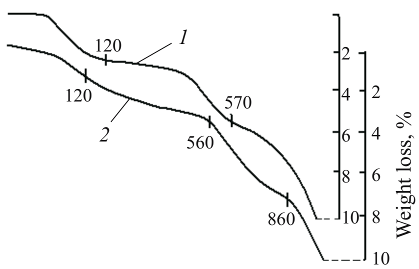

Fig. 4. Thermogravimetric weight loss curves (°C) of clay from Zapol'e deposit before treatment (*1*) and after treatment with bacterial suspension under optimal conditions (*2*).

lism are adsorbed on active sites of argillaceous particles, and the diffusion of these products is delayed, which decreases their effect.

It would be logical to assume that with increasing dispersion and plasticity of material, the drying sensitivity coefficient and the air linear shrinkage of clay samples should increase. However, the experimental results indicate that these parameters decrease. Such behavior of clay after bacterial treatment can be attributed to the fact that colloid organic compounds formed as a consequence of bacterial activity facilitate the cohesion of clay particles in drying and increase the water-retaining capacity. Furthermore, it may be assumed that under long exposure, part of the water passes from the free state to a loosely or strongly bound state due to the growing physicochemical and electrostatic forces, which additionally arise in the destruction of clay-forming minerals. Such water, which is significantly more strongly bonded in the disperse system, is removed at a higher temperature, i.e., the whole dehydration process becomes more extended in the temperature interval.

This can account for the decreased air shrinkage and drying sensitivity coefficient, which were determined according to Z. Nosova's method [5] in the course of sample drying at a temperature of 100 ± 5°C, which is insufficient for complete removal of moisture from the system. The above assumptions are corroborated by the results of the differential thermal and thermogravimetric analysis of samples of initial and biologically treated clays (using the example of clay from the Zapol'e deposit).

Thus the first endothermic effect for the biologically treated clay is smoothed and extended in a wider temperature interval (Fig. 3), since part of the water passes to a fixed state and its removals shifts toward higher temperatures. This can be attributed to an increased degree of dispersion of the clay and an increased content of particles of size below 1 μm, as well as the effect of the products of bacterial metabolism on the formation of organic colloids, which also facilitates the retaining of water.

Judging from the thermogravimetric curve (Fig. 4), the weigh losses of the considered clays occur more smoothly in a wider temperature interval, which has a beneficial effect on the drying process, since the shrinkage phenomena in the material are extended in time. This leads to a decreased drying sensitivity coefficient and makes it possible to shorten the drying cycle without the risk of crack formation.

Thus, the modification of the properties of argillaceous materials subjected to bacterial treatment occurs through activating natural microflora and also due to the products of metabolism generated by bacteria. A beneficial effect of *Bacillus mucilaginosus* bacteria on the technological properties of investigated argillaceous materials is established, which makes it possible to improve the qualitative parameters of ceramics based on these clay.

An increased degree of dispersion and plasticity of clays and a decreased linear air shrinkage and drying sensitivity coefficient make it possible to shorten the drying cycle, diminish defects in drying, intensify the sintering process, and lower the firing temperature, which helps to save fuel and power resources and increase the strength of preforms and finished products.

The use of the nontraditional method of bacterial treatment in the ceramic industry makes it possible to reduce the consumption of electricity spent on evaporation of mechanical moisture from molded preforms and expand the list of available argillaceous materials, involving local clay deposits.

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